# *Researches on the Chemistry of Coal.* Part II.—*The Resinic Constituents and Coking Propensities of Coals.*

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(Received September 14, 1921.)

## *Introduction.*

This paper embodies the results of experimental investigations, carried out during the past five years in the Fuel Laboratories of the Imperial College of Science and Technology, South Kensington, into the resinic constituents of bituminous coals and their supposed determining influence upon the coking propensities thereof.

The property of "coking," when carbonised at 900°–1000° C., is not inherent in all "black" coals, but varies from zero up to a high degree. Although, to some extent, it appears to be connected with the amount of volatile matter yielded by the dry ashless coal substance at such temperatures, the connection is by no means so direct as is sometimes supposed. Thus, whilst it may be said to be generally non-existent in coals yielding below 15 or above 45 per cent. of "volatiles," and to be at its maximum in those yielding between 15 and 30 per cent., and whereas also it gradually diminishes as the yield of "volatiles" rises above 30 per cent., yet there is no corresponding gradual diminution as the yield falls below 20 per cent. Indeed, in the region of 15–20 per cent. of "volatiles" there is an abrupt failure of coking properties; for in this region—and particularly at about 15 per cent.—are to be found not only some exceptionally strongly-coking coals, but also many that are quite devoid of the property. The reason for such an apparently sudden disappearance of coking properties in the said region remains one of the unsolved questions in the chemistry of coal.*

The attention of one of us was recently drawn to a striking instance of this kind whilst engaged upon an investigation of certain Spanish coals, which from our point of view proved to be of exceptional interest. They were representative samples, each taken from a series of three adjacent seams (called Nos. IV, V and VII respectively) of carboniferous age occurring in a range of hills running roughly E. and W. near the towns of Ponferrada and Villablino in the Province of Leon (N. Spain). The three seams in question are separated from each other by distances varying between 10 and 20 metres; and 100-lb. samples had been carefully taken from each of them under proper supervision from a fresh coal surface in the mine. No. IV was from a seam (0·6–1 metre thick), of hard-coking coal; No. V was from the next seam (varying up to 2 metres thick) of a moderately good coking coal; whilst No. VII was from a third seam (0·5 metre thick) of a semi-bituminous (or perhaps anthracitic) type quite devoid of coking properties. The ultimate compositions of the dry ashless coal substances in each case are given in Table II (Coals C, D and E), (*q.v.*); the amounts of "volatiles" at 900° C., yielded by the dry ashless coal-substances in each case, were as follows:—

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* We do not say that there is any definite point in the volatile-yield at which the coking properties suddenly fail, because there is an "overlap" between coking and non-coking coals in the range between 15 and 20 per cent.; what we rather mean is, that while with diminishing volatiles below 20 per cent. the coking properties disappear, they do so abruptly, and not gradually as they do with increasing volatiles above 30 per cent.

Table I.

| Seam. | No. IV. Hard-coking. | No. V. Coking. | No. VII. Non-coking. |
|---|---|---|---|
| Per cent. "volatiles" 900° C. | 21·70 | 22·65 | 17·80 |

The abrupt change from the well-marked coking quality of No. V to the absolutely non-coking character of No. VII in two neighbouring seams is a most interesting example of how two coals of very similar carbon, hydrogen, and oxygen contents (*vide* Table III), can yet differ absolutely as regards their coking qualities. That the change in question may possibly have been due to some igneous intrusion in or near seam No. VII, subsequent to the formation of the seams, is suggested by the occurrence of porphyritic rock in the roof of same, and also by the lower volatile yield of the coal substance on being carbonised at 900° C., as compared with the corresponding yields for the coals from the neighbouring coking seams. Some experiments with these coals were included in this research.

In this connection also mention may be made of some suggestive observations made during another investigation recently carried out at the Imperial College by one of us in conjunction with Mr. J. Roberts upon the coking properties of certain South Wales coals from seams that were "faulted" in places. In many such instances it was found that samples taken at or near the "faulted" part of a seam yielded decidedly less volatile matter, and sometimes also a denser coke, than those taken from the "unfaulted" part of the same seam, as though the coal had been partly carbonised *in situ* in the locality of the fault. In one case, such a "faulted" coal yielded 18·9 per cent. of volatiles at 900° C., as against 23·4 per cent. yielded by the normal coal from the unfaulted part of the seam. Thus the abnormal conditions of pressure and temperature, which must have prevailed locally when the "faulting" occurred, were sufficient to diminish materially the volatile contents of the coal in the region of the fault, and, at the same time, to alter its coking properties.

Some authorities have connected the coking propensities of coals with the presence in them of resinous constituents. Many years ago Carrick Anderson, in an important memoir upon the coking properties of certain Scottish coals,* ascribed them mainly, if not exclusively, to the presence of bodies of a resinoid character which are capable of extraction with dilute caustic potash solution. Later on, Bedson† found that the coking properties of a coal are destroyed when it is extracted with pyridine; such procedure, however, besides removing resins, also depolymerises the main coal-substances.

In 1913 Clark and Wheeler, by subsequently treating such pyridine extracts with chloroform, claimed to have effected "a complete, or nearly complete, separation between the resinous constituents and the degradation products of the celluloses of which coal is conglomerated,"‡ and they considered that the "binding principle" of coking coals lies chiefly in the chloroform soluble portion of their pyridine extracts, which they described as "resinic" in character. In the light of our results, however, this conclusion needs modification.

About a year ago S. R. Illingworth,§ in publishing some researches upon South Wales coals, put forward the "resinic coking theory" in a rather extreme and, as it seems to us, untenable form. He concluded that the plasticity of coking coals is due to the liquation of their resinic constituents by heat, and that, in general, 5·5 per cent. is the minimum amount of resinic matter necessary in a coal for the formation of coke and to render a coal mass plastic when heated.

The results of our researches, however, seem definitely opposed to the theory that the resinic constituents of a bituminous coal are the sole, or even the main, cause of its coking properties, although they may be a contributing factor.

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* 'Journn. Soc. Chem. Ind.,' 1898, p. 1017.

† 'Journ. Soc. Chem. Ind.,' 1908, p. 147.

‡ 'Journ. Chem. Soc.,' vol. 103, p. 1706 (1913).

§ 'Journ. Soc. Chem. Ind.,' vol. 39, pp. T. 111 and 134 (1920).

## EXPERIMENTAL PART.

### A. *Character of the Coals Investigated.*

Eight different coals (designated as A, B, ... G, H), in which the coking propensities varied from zero to a very high value, were selected for the investigation. Of these, the first two (A and B) were, respectively, the Durham coking coal and the Barnsley hard steam coal employed by Bone and Sarjant in Part I hereof.* The next three (C, D and E) were selected from the interesting series of Spanish coals already referred to, C being strongly-coking, D moderately so and E absolutely non-coking. F and G were South Wales coals; F giving a very hard and dense metallurgical coke, and G being a non-coking anthracitic variety. H was a homogeneous vitreous "jet-like" coal found in a thin bed in the Oolitic ironstone deposits of the Cleveland district of N. Yorkshire.

Incidentally also, some experiments were made upon a Nigerian black coal, which on carbonisation at 900° C. yielded a slightly coherent residue, and 45 per cent. of volatiles referred to the dry ashless coal-substance. The ultimate compositions, both of the dry coals A to H inclusive, and of their dry ashless substances, are given in Tables II and III which also record

Table II.—Ultimate Composition of the Dry Coals Investigated.

| | A. Durham coking. | B. Barnsley. | C. Spanish. | D. Spanish. | E. Spanish. | F. South Wales. | G. South Wales. | H. Oolitic. |
|---|---|---|---|---|---|---|---|---|
| Carbon ............ | 82 ·73 | 82 ·33 | 78 ·30 | 74 ·25 | 82 ·80 | 82 ·58 | 86 ·80 | 75 ·32 |
| Hydrogen ...... | 4 ·76 | 4 ·99 | 4 ·30 | 4 ·02 | 4 ·15 | 4 ·56 | 3 ·82 | 6 ·31 |
| Nitrogen ......... | 1 ·09 | 1 ·50 | 1 ·40 | 1 ·09 | 1 ·93 | 0 ·94 | 0 ·38 | 0 ·97 |
| Sulphur ......... | 1 ·28 | 0 ·70 | 0 ·75 | 1 ·35 | 0 ·72 | 0 ·47 | 0 ·96 | 0 ·67 |
| Oxygen* ......... | 7 ·38 | 7 ·72 | 6 ·00 | 3 ·04 | 3 ·85 | 7 ·59 | 5 ·52 | 6 ·72 |
| Ash ............... | 2 ·76 | 2 ·76 | 9 ·25 | 16 ·25 | 6 ·55 | 3 ·86 | 2 ·52 | 10 ·01 |
| | 100 ·00 | 100 ·00 | 100 ·00 | 100 ·00 | 100 ·00 | 100 ·00 | 100 ·00 | 100 ·00 |
| Character of coke | Hard | Moderately hard | Very dense and hard | Hard | Nil | Very dense and hard | Nil | Light porous. |
| Volatile matter expelled at 900° C. | 26 ·3 | 32 ·2 | 19 ·6 | 19 ·0 | 16 ·75 | 21 ·7 | 9 ·9 | 53 ·8 |

* As is usual in stating the results of coal analyses, the oxygen has been estimated "by difference."

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* 'Roy. Soc. Proc.,' A, vol. 96, p. 119.

Table III.—Ultimate Composition of the Dry Ashless Coal-substance.

| | A. | B. | C. | D. | E. | F. | G. | H. |
|---|---|---|---|---|---|---|---|---|
| Carbon ............ | 85 ·07 | 84 ·68 | 86 ·28 | 88 ·65 | 88 ·59 | 85·90 | 89 ·04 | 83 ·70 |
| Hydrogen ...... | 4 ·90 | 5 ·13 | 4 ·74 | 4 ·80 | 4 ·44 | 4 ·74 | 3 ·92 | 7 ·01 |
| Nitrogen ......... | 1 ·12 | 1 ·54 | 1 ·54 | 1 ·30 | 2 ·07 | 0 ·98 | 0 ·39 | 1 ·08 |
| Sulphur ......... | 1 ·32 | 0 ·72 | 0 ·83 | 1 ·61 | 0 ·77 | 0 ·49 | 0 ·98 | 0 ·74 |
| Oxygen* ......... | 7 ·59 | 7 ·93 | 6 ·61 | 3 ·64 | 4 ·13 | 7 ·89 | 5 ·67 | 7 ·47 |
| | 100 ·00 | 100 ·00 | 100 ·00 | 100 ·00 | 100 ·00 | 100 ·00 | 100 ·00 | 100 ·00 |
| Volatile matter expelled at 900° C. | 27 ·0 | 33 ·1 | 21 ·7 | 22 ·7 | 17 ·9 | 22 ·6 | 10 ·2 | 59 ·8 |

* As is usual in stating the results of coal analyses, the oxygen has been estimated "by difference."

the yields of volatile matter at 900° C. and the coking properties in each case. With regard to the latter, it may be said that coals C and F (Spanish and Welsh respectively) yielded the densest and hardest cokes of all. A represents the celebrated Durham coking coals which are employed for manufacturing the metallurgical coke used in the Cleveland blast-furnaces; D (Spanish) and B (Barnsley) gave fairly strong cokes; H (Cleveland Oolitic) gave a very light and porous coke; whilst E (Spanish) and G (South Wales anthracitic) were quite devoid of coking properties.

## B. *Effect on the Coking Properties of Extracting Coals with Various Resin-solvents.*

It was decided first of all to investigate the effect on the coking properties of bituminous coals of a thorough extraction with resin-solvents such as ethyl ether, acetone, ethyl alcohol, chloroform, benzene and xylene.

Atmospheric oxidation is known to affect the coking power of coal; and as Bone and Sarjant (*loc. cit.*) have also shown that it may seriously influence the action of solvents on the coal substance, it was necessary to carry out the extractions in an atmosphere of nitrogen. For this purpose the following special form of Soxhlet apparatus was designed, as an improvement upon that previously described by Bone and Sarjant.*

The flask F of about 450 c.c. capacity, was sealed to a wide tube, T, of 4·5 cm. internal diameter. In this tube was placed the syphoning-cup, S, which was supported by the constriction at N, and measured 10 cm. in depth by 3·3 cm. diameter. A small hole in the upper edge of the cup facilitated the lifting of it out, when necessary, by means of a hooked wire. The upper end of the wide tube, T, carried, on a ground joint, the internal water-cooled condenser, C. It was expanded a little above the joint so as to form a mercury seal, and the expansion was drawn out to a spout on one side. The effective part of the condenser was 12 cm. long by 3 cm. diameter. Just below the condenser-joint was a side tube, which was connected to a tap, R, and also to a vertical capillary tube, M, which dipped into a mercury seal, K. The connection was made either by rubber tubing or a ground glass joint.

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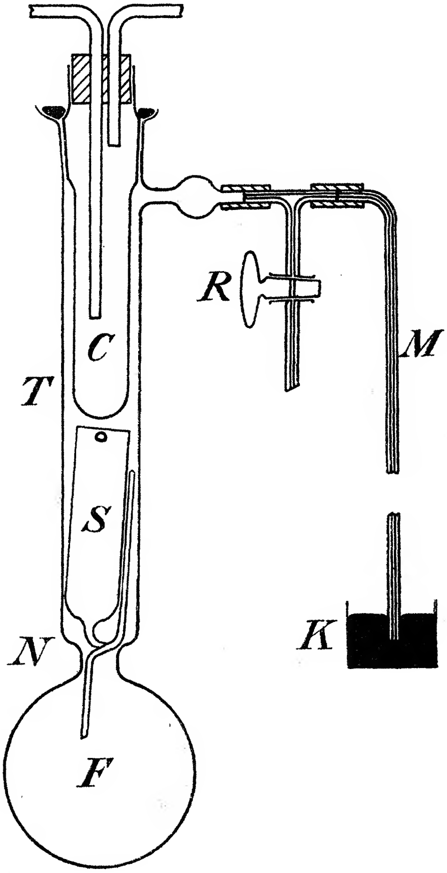
* *Ibid.*, pp. 123–127.



The advantages of such an apparatus are:—

(i) Extractions can be carried out in any desired atmosphere.

(ii) By partially evacuating the apparatus, the temperature at which extraction is carried out can, if desired, be reduced below the boiling-point of the solvent at normal pressure; this is an advantage when the substance under treatment is of an unstable nature.

(iii) Loss of the solvent is almost impossible, because its vapour is condensed before it can reach the joint or side-outlet above. For the same reason there is no risk of the extracted matter being contaminated by grease or other substance used to lute the said joint.

(iv) The insoluble residue after extraction may easily be dried without exposing it to atmospheric oxidation; for this purpose the syphoning cup is removed from the apparatus, suitably stoppered, and warmed while a current of inert gas is passed through it by way of the tail-tube.

In the first instance two series of experiments were carried out with seven of the coals, namely, A, B, C, E, F, G, and H. Dried samples of these, ground so as to pass through a mesh of 90 to the linear inch, were extracted with (*a*) acetone (b.p. 56·5°) and (*b*) benzene (b.p. 80·4°) respectively for a continuous period—in each case, of from 7 to 13 days—until no appreciable further extraction took place. The percentage amounts of extract (referred to the dry coal) are shown below:—

Table IV.—Results of Soxhlet Extraction of Coals.

| Coal. | A. | B. | C. | E. | F. | G. | H.* |
|---|---|---|---|---|---|---|---|
| Solvent— | | | | | | | |
| Acetone | 2·38 | 2·66 | 1·40 | 0·66 | 0·67 | 0·68 | 9·95 per cent. extracted. |
| Benzene | 3·27 | 1·86 | 2·04 | 1·25 | 1·18 | 0·93 | |

* In the case of this coal, the acetone-extraction was not completed in 11 days; on continuing the process for altogether 36 days 12·56 per cent. of the coal was extracted without impairing its coking properties.

So far as could be judged, the coking propensities of the five coking coals, A, B, C, F, and H, were unimpaired by the treatment; the same applied to the strongly-coking Spanish coal, C, even after it had been similarly extracted with xylene (b.p., 142°), for a period of 3 days, during which it gave 2·58 per cent. of soluble extract.

Seeing that the solvents employed in the foregoing experiments would almost certainly remove the greater part, if not all, of any free resin disseminated through the coal-substance, these results seemed to cast doubt upon the commonly accepted theory that the coking power of coals depends on their resinous constituents. In order, however, that there might be no doubt about the matter, it was decided to extract the two hard coking coals, A and B, *successively* with (*a*) ethyl ether (11 days), (*b*) ethyl alcohol (9 days), and (*c*) benzene (15 days). The results of these further experiments are given below:—

Table V.—Prolonged Soxhlet Extraction of Coals A and B, with three Resin Solvents in Succession.

| Coal. | A. | B. |
|---|---|---|
| **Ethyl ether (11 days)** | 2·20 | 2·34 per cent. extracted. |
| **Ethyl alcohol (9 days)** | 2·43 | 1·88 ,, ,, |
| **Benzene (15 days)** | 2·00 | 0·89 ,, ,, |
| Total | 6·63 | 5·11 |

In view of the fact that the resins which are known to occur macroscopically in carboniferous coal seams* are similar in solubility to contemporary resins, it seems probable that so drastic an extraction, employing successively the three solvents named, would remove all free resins from the coal-substance in each case. The residues were dried in an atmosphere of nitrogen and their coking powers compared with those of the original coals. Each yielded just as strong a coke as did the original coal. It may therefore be concluded quite definitely that the coking properties of these coals do not depend upon the presence in them of free resins.

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* *Vide* W. A. Bone, 'Coal and its Scientific Uses,' pp. 78–80.

With regard to the characters of the extracts obtained in the last-named experiments, it may be remarked that: (*a*) those removed by ether were brownish-yellow substances of the consistence of vaseline and strongly fluorescent in solution; (*b*) the alcohol-extracts were dark brown brittle masses suggesting resins in appearance; whilst (*c*) the benzene-extracts were soft dark brown solids resembling natural bitumens, and strongly fluorescent in solution. The amounts of such extracts obtained in the experiments were insufficient to allow of more than a general examination of them being made.

It is, of course, well known that the extraction of coal with certain basic solvents, such as pyridine, completely destroys the coking power. Such result, however, is not due to the mere removal of resins, but rather to the depolymerising action of the pyridine upon the coal-substance.* We were therefore led to try the effect of extracting the two hard coking coals, A (Durham) and C (Spanish), with symmetrical tetrachlorethane ($CHCl_2—CHCl_2$), in an atmosphere of nitrogen at ordinary pressure. This liquid is not only a powerful solvent for resins, but it also, as we found, attacks and decomposes the coal-substance. On making the experiments, it was found that the coking powers of the two coals in question were utterly destroyed by only one day's Soxhlet extraction with this solvent. Hydrogen chloride was evolved during the process, and some water was formed by decomposition of the coal-substance. The residues contained chlorine, and they actually weighed more than the coal originally taken.

Some similar extraction experiments were made with trichlorethylene ($CHCl:CCl_2$, b.p. 85°), and also with chloroform (b.p. 61°), as solvents. In the case of trichlorethylene, no hydrogen chloride was evolved during the actual extraction, but it was eliminated when the residues were carbonised. The residues, however, all coked strongly. Chloroform had a still milder action on the coals; the amounts of extractive matter removed by it in three to five days' Soxhlet extraction were as follows:—

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* See Bone and Sarjant, *loc. cit.*, p. 132.

Table VI.—Soxhlet Extraction of Coking Coals by Chloroform.

| Coal. | Percentage extract. |
|---|---|
| A. (Durham) | 3·27 |
| B. (Barnsley) | 5·13 |
| D. (Spanish) | 3·48 |
| F. (Welsh) | 1·20 |

No hydrogen chloride was evolved, and the coking powers of the residues were in each case unimpaired. It should here be mentioned, however, that, at one stage of our inquiry, experiments were tried upon the effect of passing a stream of chloroform vapour over the Durham and Spanish coals A and D, maintained at temperatures between 220° and 270° C. It was found that hydrogen chloride appeared at 220°, and that its evolution increased rapidly as the temperature was raised beyond that point. It was evident that the coal-substance was being attacked chemically, with the result that the coking power of the Durham coal had deteriorated somewhat, whilst that of the Spanish coal was entirely destroyed. Control experiments, in which the coals were similarly heated in a current of nitrogen, showed no deterioration of the coking power.

We conclude from this series of experiments:

(1) That the coking propensities of coals are not mainly due to the presence in them of free resins; but

(2) That they may be destroyed by the action of any solvent or vapour which will either depolymerise the coal-substance (as pyridine does) or radically alter it by chemical interaction (as is the case with tetrachlorethane).

### C. *A Method of Isolating Coal-Resin.*

During the investigation it had become evident that rather a large quantity of a coal must be extracted in order to obtain from it enough of the resinic constituents for a thorough examination of them. The usual Soxhlet method was manifestly unsuitable for such purpose; also an extraction of the coal by pyridine alone was objectionable, on account of the depolymerising action of this solvent upon the non-resinous matter. We had, therefore, to devise some other process for the isolation of resins from coal which would minimise this disadvantage. After numerous trials, we were finally led to employ a mixture of equal parts of pyridine and amyl alcohol as a more suitable medium, and to substitute for the Soxhlet apparatus a two-gallon metal canister fitted with a reflux condenser, and also with a tube reaching nearly to the bottom through which a current of inert gas (*e.g.*, nitrogen) could be passed so as to avert oxidation during the extraction process.

The experimental procedure was substantially as follows:—

One kilogramme of the dried coal, ground to pass a 60-mesh sieve, was added to 3 litres of a mixture of equal volumes of pyridine and amyl alcohol contained in the canister. The contents were boiled for periods varying from 10 to 60 hours, a slow stream of nitrogen being maintained through the apparatus meanwhile. According to our experience, the employment of such a mixture as the extracting medium greatly mitigates the "unbuilding" action of undiluted pyridine upon the coal-substance* without materially impairing its solvent action upon the resinic constituents thereof. At the end of the said extraction period the solution was separated from the residue, either by filtration on a Buchner funnel at the pump, or by sucking off the solution through an alundum cylinder immersed in it. The latter method was the more expedient, because it minimised exposure to the air. The resulting clear solution was then concentrated to about one-fifth of its bulk by distillation. The remainder of the mixed solvent was removed by distillation, under 20 mm. pressure, in a special form of steam-jacketed vacuum still.

The crude extract thus obtained was a brownish black magma. It varied in amount according to the time of extraction allowed; but subsequent investigation showed that the amount of resin finally obtained from it did not vary materially with the time taken, indicating that such resin had been mostly extracted during the first 10 or 20 hours.

The first step in the purification of the crude extract consisted in dissolving out its resinic part by boiling it with ethyl ether in a reflux apparatus. The ethereal solution was washed with dilute sulphuric acid, to remove last traces of pyridine, and then with water. It was next distilled down to small bulk, and the concentrated solution transferred to an apparatus where it was steam-distilled for 6 hours or more, in order to remove all traces of amyl alcohol. Whilst still hot, the contents of the apparatus were poured into a basin, in which they were allowed to cool, when a brittle button of resinous appearance was obtained. This was roughly dried between filter paper and afterwards powdered and completely dried *in vacuo* over sulphuric acid. It will be referred to hereafter as Resin-extract A.

The portion of the pyridine-amyl alcohol extract which was insoluble in ether was non-resinous; it could be further resolved by normal alcoholic potash solution into (i) an alkali-soluble part; and (ii) an alkali-insoluble part. For the further examination of these products, see below.

*Purification of the Resin-extract A.*—The yield of Resin-extract A from the Durham and Barnsley coals (the only ones tried) varied from 1·27 to 2·75 per cent. of the weight taken. The extract softened at about 60° C., and on analysis it proved to be free from sulphur and nitrogen. The ultimate composition of one specimen derived from the Barnsley coal was found to be :—

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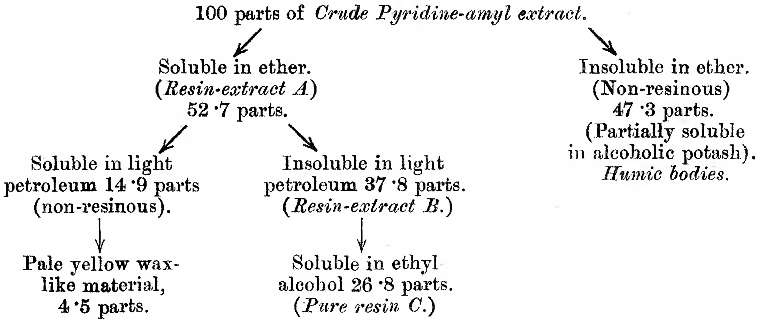
* *Vide* Bone and Sarjant, *loc. cit.*, p. 132.

| | Per cent. |
|---|---|
| Carbon | 80·13 |
| Hydrogen | 7·13 |
| Oxygen (by difference) | 12·74 |
| | 100·00 |

Further investigation proved the material to be a mixture, and it was therefore separated into two portions by extraction with light petroleum (b.p. 40°–60°) in a Soxhlet apparatus. This solvent removed a non-resinous waxy constituent, which, on subsequent refining by means of sulphuric acid, was finally obtained as a pale yellow substance, resembling soft paraffin in appearance. The residue, insoluble in light petroleum, was resinous in character (Resin-extract B); it was further purified by solution in cold ethyl alcohol, yielding a pure resin (Resin C).

The following scheme shows the results of subjecting the Barnsley coal B to the treatment outlined above :—


100 parts of *Crude Pyridine-amyl extract.*
Soluble in ether.
(*Resin-extract A*)
52·7 parts.
Insoluble in ether.
(Non-resinous)
47·3 parts.
(Partially soluble in alcoholic potash).
*Humic bodies.*
Soluble in light petroleum 14·9 parts (non-resinous).
Insoluble in light petroleum 37·8 parts.
(*Resin-extract B.*)
Pale yellow wax-like material, 4·5 parts.
Soluble in ethyl alcohol 26·8 parts.
(*Pure resin C.*)

There have thus been isolated from the coal :—

(1) A non-resinous wax-like substance, soluble in light petroleum.

(2) A resin, insoluble in light petroleum, but soluble in alcohol.

(3) Non-resinous substances of "humic" type, insoluble in light petroleum. These will now be further described as follows :—

(1) *The non-resinous wax-like substance* amounted in all to about 0·35 per cent. of the original coal. On purification with sulphuric acid it yielded a pale yellow substance with the appearance of a soft paraffin, which did not

absorb bromine. This substance was free from nitrogen and sulphur, and on analysis was found to contain :—

| | Per cent. |
|---|---|
| Carbon | 86·00 |
| Hydrogen | 10·80 |
| Oxygen (by difference) | 3·20 |
| | 100·00 |

The substance was soluble in ether, chloroform and most other organic solvents, its solutions having a characteristic green fluorescence. The amount isolated was too small to permit of further investigation.

(2) *The Resin.*—This was a translucent solid of deep red colour in mass, but amber-yellow when powdered. It had a conchoidal fracture and was completely soluble in ethyl ether, alcohol, acetone, benzene, acetic acid and chloroform; but it was insoluble in light petroleum. It began to soften at a temperature just above 100° C. The resin was free from nitrogen and sulphur, its ultimate composition being as given below. It resembled a "resene" in its chemical inertness. Two determinations of its molecular weight by the ebullioscopic method (Beckmann apparatus), using ethyl alcohol as solvent, gave (i) 453·0 and (ii) 450·7. These values, and the ultimate composition agree well with the empirical formula $C_{31}H_{32}O_3$ (Mol. Wt. 452·0) :—

| | Found. | Calculated for $C_{31}H_{32}O_3$. |
|---|---|---|
| Carbon | 82·15 | 82·30 per cent. |
| Hydrogen | 7·11 | 7·08 " |
| Oxygen (by difference) | 10·74 | 10·62 " |
| | 100·00 | 100·00 |

The total amount of the purified resin finally isolated from the two coking coals used did not much exceed 1 per cent. of their weight; and we think this figure (or perhaps something between it and 2 per cent.) may be accepted as an approximately correct indication of the proportion of true resin in such coals.

(3) *The Humic Substances.*—These constituted the portion of the crude pyridine-amyl alcohol extract which was insoluble in ether. They may also be obtained (as we found later) by extracting coal with pyridine alone, and then treating the pyridine extract, first with ether to remove the resinous and waxy substances, and then with chloroform, which dissolves these humic bodies. It may be remarked that the term "humic" is here used as a

convenient designation for these compounds, because it is a generic term, denoting the brown or black products resulting from the condensation or dehydration of celluloses and carbohydrates generally under the influence of acids or bacterial agencies. And there is strong reason for believing, as will appear later, that the substances which we are now discussing are chiefly of cellulosic origin although they also contained some nitrogenous material. From the method of their isolation, it would appear that these humic bodies constituted a considerable part of the "resinic constituents" which Clark and Wheeler obtained by the pyridine-chloroform extraction method referred to in the introduction to this paper.

The Durham coal yielded about 4 per cent. of its weight of these humic bodies. They formed a deep brown mass, chocolate-coloured when finely powdered, and were partially soluble in an alcoholic solution of potash. The resulting solution was colloidal, and on saturating it with either hydrogen chloride or carbon dioxide, a brown flocculent precipitate was thrown down, which when dried had the composition :—

| | Per cent. |
|---|---|
| Carbon | 76·25 |
| Hydrogen | 5·15 |
| Oxygen (by difference)* | 16·85 |
| Nitrogen | 1·75 |
| | 100·00 |

A noteworthy point about this acidic substance was that, when the flocculent precipitate was freshly filtered off, it formed a bulky dark-coloured opaque jelly; but when the latter was subsequently dried it shrank enormously, finally leaving a brittle lustrous black structureless mass, with conchoidal fracture, resembling the Oolitic coal, H, or those bright bands in bituminous coals which Stopes† has named "vitrain." This characteristic behaviour suggests that such "vitrain" may have been formed from a colloidal gel, and we propose in future experiments to explore further this aspect of the matter.

Both the humic bodies as a whole, and also the acidic part of them described above, when slowly heated in an apparatus similar to that used by Hollings and Cobb,‡ showed a strongly exothermic decomposition within the temperature range 275° to 375° C. Cellulose itself showed a similar evolution of heat at about 350°, as indeed Hollings and Cobb had previously proved. These facts strongly suggest that the "humic" constituents here in question are chiefly of cellulosic origin; but the further development of this important aspect of the question is reserved for a future communication.

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* The oxygen figure would include a little sulphur, which was not separately determined, owing to the small amount of material at our disposal.

† 'Roy. Soc. Proc.,' B, vol. 90, p. 470 (1919).

‡ 'Journ. Chem. Soc. (Trans.),' 1915, p. 1106.

### D. *Experiments on the Coking Principle of Coals.*

The constituents of coal described above having been thus separated, and to some extent characterised, it remained to test their relative influences in the formation of coke. This was done in the following manner:—

Each of the substances was mixed in varying proportions with a dry coke which had previously been prepared at 900° C., and ground to pass a sieve of 30 meshes to the inch. Intimate mixture was assured either by grinding the materials together in an agate mortar or by dissolving the coal-constituent under examination in a suitable solvent, absorbing the solution on a weighed quantity of the coke-dust and drying off the solvent at a gentle heat. Ten grammes of every such mixture were then placed in a cylindrical iron vessel of about 1 inch internal diameter. The bottom of this vessel was closed by an iron plate firmly held in position by screws, and into the top was passed a solid iron cylinder, weighing about 100 grm., and making a good sliding fit into the coking chamber, so as to hold the charge together, while allowing any gaseous products to escape, during the subsequent heating operation.

The vessel thus charged was placed at once into an electric muffle furnace at 850–900°, and left there for 6 or 8 minutes, by which time all smoke and flame were spent. It was then taken out and allowed to cool. Using 9 grm. of coke-dust and 1 grm. of each ingredient (*i.e.*, 10 per cent. mixtures), the following results were obtained:—

(1) The non-resinous waxy material, soluble in petroleum ether, gave a pulverulent residue.

(2) The resin gave a coke-like product firm enough to be tested as to its crushing strength.

(3) The alkali-soluble humic material gave a similar coke-like product about equal in strength to that obtained with the resin.

(4) The chloroform-soluble humic material gave a good firm "coke."

(5) The portion of the pyridine extract which was insoluble in chloroform gave, in 10 per cent. mixtûre, a pulverulent residue. Alone, or in 50 per cent. mixture with coke-dust, it gave a weakly coherent residue.

The crushing strengths of various "cokes" prepared in the above manner were now measured in a cement-testing machine. For this purpose the end faces of the specimens were ground down so as to give cylindrical blocks exactly 18 mm. high, on which the tests were performed. The following figures show the relative crushing strengths, in lbs. per square inch, of specimens prepared from the intimate mixtures of coke-dust with (*a*) the untreated Durham coal; (*b*) the "humic" material obtained from the Durham coal; and (*c*) a similarly prepared humic extract from the slightly coking Nigerian coal mentioned in the introduction to this paper.

Table VII.—Crushing Strengths of the "Cokes."

| Percentage of binding ingredient used. | Binding material employed. | | |
|---|---|---|---|
| | Durham coking coal. | Humic matter extracted from | |
| | | Durham coal. | Nigerian coal. |
| 5 | — | 100 | |
| 10 | Pulverulent | 1. 100<br>2. 150 | 1. 60<br>2. 125 |
| 20 | 125 | 1. 400<br>2. 420 | 1. 225<br>2. 300 |
| 30 | 260 | | |
| 40 | 1. 325<br>2. 550 | | |
| 50 | 1. 190<br>2. 175 | | |

No test could be obtained with the mixtures containing 30 per cent. of the humic material, because they intumesced to such an extent as to be forced out of the coking vessel. Both the pure coal-resin, and the alkali-soluble portion of the humic material,* had a considerable cementing power, 10 per cent. mixtures of them giving crushing tests of 130 and 125 respectively. But, inasmuch as the resin only constitutes about 1 per cent. of the coals which we have so far tested, it can hardly play a great part in the formation of coke from them.

It will be seen from the figures above quoted that, what we have termed the "humic" extracts (even that prepared from the Nigerian coal) have a strong cementing effect; but whereas the weakly-coking Nigerian coal yielded only 1·7 per cent. of these bodies, the strongly coking Durham coal yielded 4 per cent. of them.

We do not wish to imply that the coking propensities of the two coals depended simply and solely upon these figures; because it may be that such "humic" extracts as were used in the experiments did not exist in the free state in the original coal, but were liberated by the action of pyridine upon it.

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* Obtained by acidifying its alcoholic potash solution, and subsequently collecting the resulting reddish-brown flocculent precipitate by filtration at the pump, washing it with cold dilute alcohol, and finally drying it *in vacuo* over sulphuric acid.

Nevertheless, though present in the coal possibly in a state of loose combination (or polymerisation), they may well be liberated, during the chemical upheaval that takes place during carbonisation, and by their subsequent decomposition play a determining part in the cementation of the residual coke.

It is therefore probable, as Clark and Wheeler surmised, that the "binding principle" of coking coals lies chiefly in the chloroform-soluble portion of their pyridine extracts; but, according to our experiments, it is not "resinic" in origin. It appears rather to consist of a series of "humic" transformation products of cellulose, of varying complexity. The simpler members of this series are soluble both in chloroform and in alcoholic alkali; and they are also easily fusible. Indeed some of the most soluble, obtained as a yellow powder by fractional precipitation from hot alcohol, melted below 100° C. Further up the series these substances become insoluble, even colloidally, in alkali, though they are still soluble in chloroform; also, their temperature of fusion rises so as to approach nearly that of their decomposition. The members up to this point, apparently, are the chief binding agents in coke-formation, and although not necessarily present in the free state in the raw coals, they exist in a state of loose combination therein, from which they are liberated by a moderate degree of heat. Higher still up the series there are more complex bodies of cellulosic origin which are insoluble in chloroform, though still extractable by pyridine. These, and the yet more complex substances insoluble in pyridine, decompose without fusion, and thus have little or no binding power.

### *Summary and Conclusions.*

The results of the investigation, taken as a whole, lead to the following conclusions:—

(1) That strongly-coking bituminous coals may be extracted for prolonged periods by organic resin-solvents without impairing their coking propensities.

(2) That the pyridine-chloroform method of extracting coals does not, as Clark and Wheeler have claimed, effect "a complete, or nearly complete, separation between the resinous constituents and the degradation products of the celluloses of which coal is conglomerated"; but that, on the contrary, it yields an admixture of resins with a predominance of non-resinous substances, which latter are chiefly of cellulosic origin, and have been provisionally designated "humic" bodies in this paper.

(3) That resins may be extracted and isolated in a pure condition from such coals by means of pyridine-amyl alcohol treatment, following by successive treatments with ethyl ether and light petroleum, in the manner described in Section C hereof, but that these resins probably do not normally much

exceed 1 per cent. of the coal-substance, and, although they may be a contributory, are not usually the chief cause of the coking propensities of coals.

(4) That there can also be obtained from such coals, by the special pyridine or pyridine-amyl-alcohol treatments described in Section C hereof, a series of non-resinous substances, which are, for the most part, insoluble in ether but soluble in chloroform, and that the yield of such bodies may amount to as much as 4 per cent (or even more) in the case of strong coking coals.

(5) That the aforesaid non-resinous substances on being heated, out of contact with air, give a strong exothermic reaction between 275° and 375° C. accompanied by the elimination of water, which behaviour resembles that of cellulose, showing them to be chiefly cellulosic in type and origin.

(6) That the coking propensities of coals are principally due to the presence, or the formation in them by heat, of such non-resinous substances of cellulosic origin as aforesaid, whose fusion temperatures are below those at which they undergo rapid decomposition.

(7) That the yet more complex substances, also of cellulosic origin, which form the main portion of the coal-substance, but which decompose without fusion, have little or no direct influence upon its coking propensities.

In conclusion, it should be stated that the participation of one of us (A. R. P.) in the investigation was made possible by a grant from the Department of Scientific and Industrial Research, to which due acknowledgment is hereby gladly made, and that the research is being continued with such aid. We also desire to acknowledge the valued assistance of Mr. A. R. Godfrey, A.R.C.S., in connection with the new method of isolating coal-resin described in Section C of the paper. Finally, we are much indebted to Messrs. Minero Siderurgica de Ponferrada, S.A., of Madrid, and to Mr. H. M. Morgans (formerly their Engineer), for their kind permission to include in this paper the references to the interesting Spanish coals upon which we experimented.